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Preparation and characterization of lake pigments from sappan wood using Thai local clays

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Abstract

Thai local clays: Munpoo clay (**MC**) and Dindang clay (**DC**) were utilized as the adsorbents for preparation of the lake pigments from sappan wood. The lake pigment which was prepared by using **MC** as the adsorbent (**L-MC**) appeared reddish-brown while a deeper reddish-brown color of the lake pigment (**L-DC**) was obtained by using **DC** as the adsorbent. Characterization of **MC**, **DC**, **L-MC**, and **L-DC** was accomplished by XRD, SEM, FT-IR, BET, TGA and UV-Vis DRS. The effects of adsorbent dosage, pH of sappan wood extract and time on the adsorption were also investigated. The results revealed that silicon oxide and aluminium silicate hydroxide were identified as the main component of **MC** and **DC**. **L-MC** and **L-DC** exhibited similar XRD pattern compared to **MC** and **DC** but with the lower crystallinities. Brazilein from sappan wood could not only form complexes with Al and Si on the surface of the clays but also interact with clay surface via electrostatic interactions, which led to the reddish-brown color of **L-MC** and **L-DC**. Furthermore, our method could benefit and promote uses of natural clays in the production of lake pigment which could be used in paints and textile dyeing processes.

1. Introduction

In the Northeast of Thailand, there are many types of natural clays found largely in the soil [1]. The quality of the soil in this area is rather low because 80% of this area was occupied by sandy soil which lacks fertility [2,3]. As a result, it cannot be used for economic crops cultivation without proper irrigation and application of fertilizers [4]. Munpoo clay (**MC**) and Dindang clay (**DC**) are two types of natural clays from Kamchanode village, located in Ban Dung sub-district, Bandung district, Udorn Thani province in the Northeast of Thailand, where most of the villagers are rice farmers, salt farmers, and fish cultivators. **MC** is a fine pale yellow clay found on the top of the soil or at 50-centimeter depth in the rice field. **DC** can be found under the high-land ground at about 1 meter in depth from the ground. **DC** is a mixture of pale brown fine particles and pebbles. The land, where **MC** and **DC** can be found, are rather useless and not suitable for growing crops due to lack of nutrition. Therefore, in this study, the characteristics and properties of **MC** and **DC** were investigated in order to improve their qualities to enhance their utilization. Indeed, several natural clays were characterized and analyzed for wider their applications [5-8].

The use of natural dye and natural lake pigments as colorants in the production of cosmetics, paints, and inks has become more attractive to industries in recent years due to health awareness and environmental impact of synthetic dyes [9-12]. Lake pigments can be prepared by several methods including precipitation and adsorption methods [13-15]. The precipitation method involves the precipitation of salts with fixed dye-metal ratios, while the adsorption method requires electronic interaction, van der Waals interaction between the dye and the surface of the adsorbent [10,16,17]. For the preparation of lake pigments using the adsorption method, clay is one of the interesting adsorbents due to its unique properties such as large surface area, small particle size, and high surface charge [18-20]. There were many reports of the utilization of pure clays including kaolinite, montmorillonite as adsorbents for the preparation of lake pigments [21-23]. However, the use of natural clay for this application has rarely been explored.

In this work, two Thai local clays: Munpoo clay (**MC**) and Dindang clay (**DC**) from the Northeast of Thailand were utilized as adsorbents in the preparation of lake pigments using the adsorption method. Sappan wood which contained reddish dye named brazilein (shown in Figure 1) was chosen as a natural coloring agent. The characteristics and properties of **MC** and **DC** and lake pigments (**L-MC** and **L-DC**) were also explored using several techniques. Moreover, adsorption parameters including adsorbent dosage, pH and time were investigated. These results could promote the use of natural clay as well as increase the value of natural clay and benefit the community in term of optional income.

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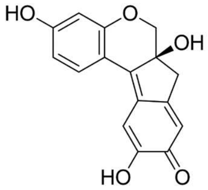


Figure 1. Molecular structure of brazilein.

2. Experimental

2.1 Materials

Two types of Thai local clays: Munpoo (**MC**) and Dindang clay (**DC**) from Kamchanode village, located in Ban Dung sub-district, Bandung district, Udorn Thani province in the Northeast of Thailand were used as supporting materials for the preparation of lake pigments from sappan wood. The clays were heated at 80-90°C for 2 h and sieved with a 120 mesh size Nylon sheet to give a fine clay powder. Sappan wood was from the local market in Bangkok, Thailand. To prepare sappan wood extracts, sappan wood was heated in water with 1:5 w/w ratio for 5 h then filtered.

2.2 Preparation of lake pigments and adsorption experiments

Lake pigments from sappan wood were prepared using the adsorption method. The adsorption experiments were conducted by mixing clays 4% w/v with sappan wood extract under magnetic stirring for 3 h, followed by filtration. The lake pigments were washed three times with distilled water and ethanol and dried in the oven at 80°C for 24 h. After that their diffused reflectance UV-Vis spectra (UV-Vis DRS) and CIELAB values (L*, a*, b*) were measured and compared. In CIELAB color system, "L" describes lightness, "a" measures redness (+ve) or greenness (-ve) and "b" measures yellowness (+ve) or blueness (-ve). Additionally, adsorption parameters including adsorbent dosage (1-10% w/v), initial pH of sappan wood extracts (pH 3-11) and times (10-180 min) were investigated.

2.3 Characterizations

The crystal structure was studied by X-ray diffraction (XRD) patterns obtained from a Rigaku MiniFlex II X-Ray diffractometer with Cu Kα radiation (1.5406 Å) from 20° to 80° (2θ). Using Fourier-Transform Infrared spectrophotometer (Thermo Scientific Nicolet 6700), Fourier-transformed infrared (FT-IR) spectra were recorded in the range 400-4000 cm^{-1} with the KBr pellet technique. Quantachrome instrument in N_2-adsorption mode was employed to determine BET surface areas, while the morphologies and elemental analysis were explored using a scanning electron microscopy (SEM, JEOL model JSM-7800F) with energy dispersive X-ray spectroscopy (EDS) attached. A Shimadzu UV-2401 spectrophotometer was used to determine the optical absorption property and band gap energy. The colorimetric CIELAB measurement was carried out using a Cary 60 UV–Vis spectrophotometer with a fiber optic coupler. The thermal analysis was also conducted using a Thermogravimetric Analyzer (TGA) (Pyris 1, Perkin Elmer, USA) by heating the samples (ca. 3-5mg) from 50-600°C at a 20°C min^{-1} heating rate.

3. Results and discussion

3.1 Characterization of MC, DC, L-MC, and L-DC

As can be seen in Figure 2, **MC** and **DC** were pale yellow and pale brown, respectively, while **L-MC** (lake pigment prepared using **MC** as adsorbent) and **L-DC** (lake pigment prepared using **DC** as adsorbent) were reddish brown and deep reddish-brown, respectively. Using the XRD technique, the composition of **MC**, **DC**, **L-MC** and **L-DC** were investigated and the results were shown in Figure 3. It was found that all diffraction peaks of **MC** were composed of silicon oxide (SiO_2), aluminium silicate hydroxide ($Al_2Si_2O_5(OH)_4$) and potassium aluminium silicate ($KAlSi_3O_8$), while the diffraction peaks for **DC** were composed of silicon oxide (SiO_2), potassium aluminium silicate ($KAlSi_3O_8$), montmorillonite ($Na_{0.3}(Al,Mg)_2Si_4O_{10}(OH)_2 \cdot 8H_2O$ and $Ca_{0.2}(Al,Mg)_2 Si_4O_{10}(OH)_2 \cdot xH_2O$). Both **MC** and **DC** also had the FeO(OH) peaks at 2θ=21, 26, 36, 63. [24] Moreover, comparison of the XRD diffraction patterns of **MC** and **DC** to those of **L-MC** and **L-DC** revealed that their XRD diffraction patterns were similar. Additionally, the crystallinities of **L-MC** and **L-DC** were much lower than those of **MC** and **DC**. This was attributed to the adsorption of brazilein on the surface of clay which induced bulk phase change. [25]

Figure 2. **MC** and **DC** compared with **L-MC** and **L-DC**.

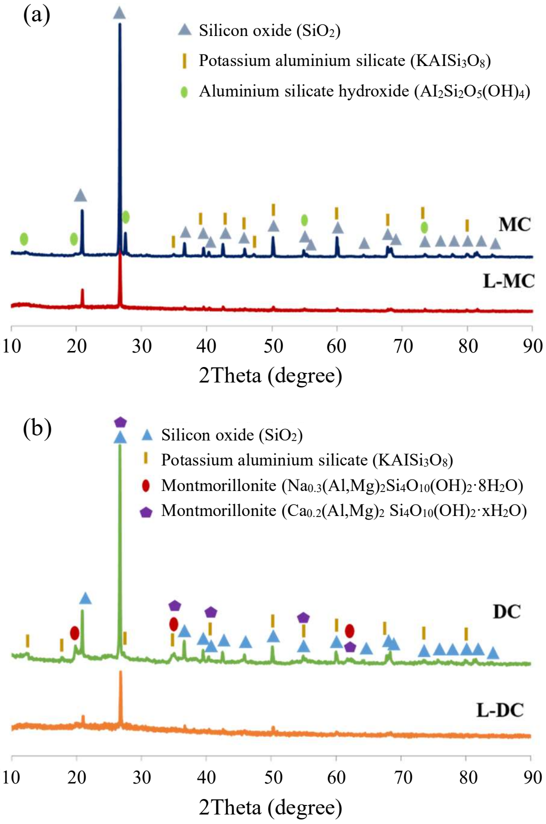


Figure 3. (a) XRD diffraction patterns of **MC**, **L-MC** and (b) XRD diffraction patterns of **DC**, **L-DC**.

The morphologies and element compositions of **MC** and **DC** were further evaluated by SEM technique and EDS analysis. Figure 4 revealed that most of the **MC**, **DC**, **L-MC**, and **L-DC** particles had significant sheet-like structures with high agglomeration to larger sizes, indicating that dye loading did not affect the morphologies of clays. Table 1 demonstrated the elements with their %weight observed in **MC**, **DC**, **L-MC**, and **L-DC**. The presence of Si, Al, Mg, K, Fe, Ca, Ti, C, and O was consistent with the XRD results.

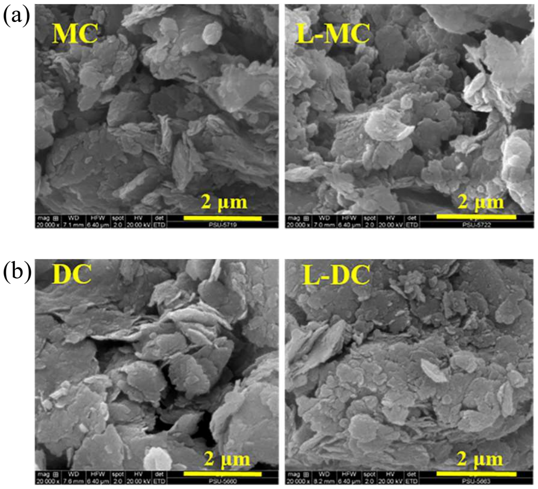


Figure 4. (a) SEM images of **MC**, **L-MC** and (b) SEM images of **DC**, **L-DC**.

Using FT-IR spectrometer, the surface chemical compositions of **MC**, **DC**, **L-MC**, and **L-DC** were investigated. As illustrated in Figure 5 and Table 2, the FT-IR spectra of **MC** and **DC** were dominated by a broad band at around 1098-1107 cm^{-1}, which was characteristic of the Si-O asymmetric stretching. Additionally, there were characteristic peaks of SiO_2 at 797 cm^{-1} and 467 cm^{-1}, corresponding to Si-O-Si stretching vibrations and Si-O-Si bending mode interaction, respectively [9,17,23,25,26]. The bands at 2924, 2853 and 1031 cm^{-1} were attributed to aliphatic C-H and C-O stretching vibrations, respectively. The bands near 3436 and 1630 cm^{-1} were attributed to stretching and bending vibrations of the O-H bond, respectively. Furthermore, the comparison of the FT-IR spectra of **L-MC** and **L-DC** with those of **MC** and **DC** revealed that their spectra were similar. This may be due to the low amount of brazilein adsorbed on the surface of clays, and the overlapping of the characteristic peaks of brazilein [27] and clays.

Table 1. Elements and their weight % observed in **MC**, **DC**, **L-MC**, and **L-DC**.

Element	**Weight %**			
	MC	**DC**	**L-MC**	**L-DC**
C	2.39±1.11	2.39±0.73	4.02±1.35	3.58±1.25
O	50.30±2.48	47.97±3.16	51.66±1.81	48.39±1.48
Mg	1.15±0.12	2.09±0.20	0.96±0.17	1.76±0.44
Al	16.98±1.57	12.54±1.64	11.86±5.19	9.17±3.97
Si	21.07±0.54	23.72±1.62	26.48±6.06	28.72±5.63
K	1.68±0.34	1.15±0.60	1.15±0.30	2.30±0.94
Ca	0.32±0.06	0.94±0.19	-	0.81±0.23
Ti	1.02±0.15	1.12±0.28	-	0.71±0.11
Fe	5.11±0.86	6.00±2.66	3.87±3.13	4.56±1.48

Table 2. FT-IR vibration assignment of **MC**, **DC**, **L-MC**, and **L-DC**.

Vibration assignment	**Wavenumber, cm^{-1}**			
	MC	**DC**	**L-MC**	**L-DC**
$\nu_{Si–O–Si}$	796	797	795	797
$\nu_{Si–O}$	1107	1099	1110	1098
$\nu_{C–O}$	1031	1032	1034	1031
$\nu_{C–H}$	2924	2924	2924	2924
$\nu_{O–H}$	3436	3432	3435	3427
$\delta_{Si–O–Al}$	535	527	535	527
$\delta_{O–H}$	1630	1637	1624	1634
$\delta_{Si–O–Si}$	467	470	470	467

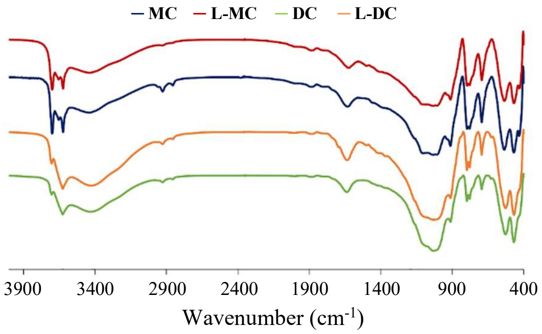


Figure 5. FT-IR spectra of **MC** and **DC** compared to those of **L-MC** and **L-DC**.

The nitrogen adsorption-desorption isotherms and pore size distribution of **MC** and **DC** were also explored. The results revealed that **MC** and **DC** appeared to be type IV (BDDT classification), indicating mesoporous structure. The calculated specific surface areas of **MC** and **DC** were 22.21 m^2·g^{-1} and 29.97 m^2·g^{-1}, respectively. For the pore size distribution, **DC** showed narrow pore size distribution with a pore size of around 18 nm, whereas **MC** exhibited bimodal pore size distribution with pore sizes of around 20-30 nm and 60-70 nm. Additionally, the pH drift method was employed to determine the pH$_{pzc}$ values of **MC** and **DC**. It was found that the pH$_{pzc}$ values of **MC** and **DC**, determined from the interception point between the data curve and the straight line of pH$_i$ = pH$_f$ (blue line), were 7.60 and 7.94, respectively.

In addition, the thermal stability of **MC**, **DC**, **L-MC**, and **L-DC** was investigated and their thermogravimetric analysis results were demonstrated in Figure 6. **MC**, **DC** exhibited two mass loss stages observed at 50-250°C and 450-550°C corresponded to the loss of water and hydroxyls, respectively. On the other hand, **L-MC** and **L-DC** exhibited three mass loss stages observed at 50-250°C, 250-460°C and 460-600°C, corresponded to the loss of water, organic matter (expected to be brazilein) and hydroxyls, respectively. This indicated that weight % of organic matter, mainly brazilein from sappan wood extract in **L-MC** and **L-DC** were 3.8% and 2.1%, respectively.

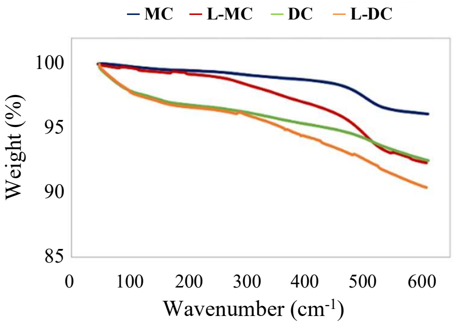


Figure 6. Thermogravimetric curves of **MC**, **L-MC**, **DC**, and **L-DC**.

3.2 Adsorption experiment results

3.2.1 Effect of adsorbent dosage on the adsorption

To explore the effect of the amount of **MC** and **DC** on the adsorption of sappan wood extract, adsorption experiments were carried out using the adsorbent dosage of 1-10% w/v at pH 5.47 (pH of sappan wood extract). Table 3 showed that when higher amounts of **MC** were used, pH of sappan wood extracts after adsorption decreased from 5.57 to 4.46 while the pH of sappan wood extracts after adsorption increased from 5.57 to 7.23 with the increasing amounts of **DC**. Moreover, sappan wood extract is pH sensitive [28], resulted in the change of the color and the wavelength of the maximum absorbance of the sappan wood extract after the adsorption. Hence, the effect of the amount of adsorbent dosage on the adsorption was observed from the comparison of UV-Vis DRS and CIELAB of the lake pigments.

As can be seen in Figure 7a and 7c, the maximum diffuse reflectance of **L-MC** and **L-DC** were at 520 and 509 nm, respectively. With the increasing of clay dosages, a small decrease of the absorbance at 520 nm of **L-MC** was observed while the absorbance at 509 nm of **L-DC** was similar (Figure 7b and 7d). This indicated that **DC** has a lower adsorption ability than **MC**. Table 4 also demonstrated the change of the color and CIELAB of lake pigments upon the increasing amount of clays.

Table 3. pH of sappan wood extracts after the adsorption using the various dosage of **MC** and **DC**.

Adsorbent dosage (% w/v)	**pH of sappan wood extracts after adsorption**	
	MC	**DC**
1%	5.23	5.93
2%	5.04	6.68
3%	4.88	6.68
4%	4.74	6.71
5%	4.68	6.91
6%	4.49	6.94
8%	4.49	7.07
10%	4.46	7.23

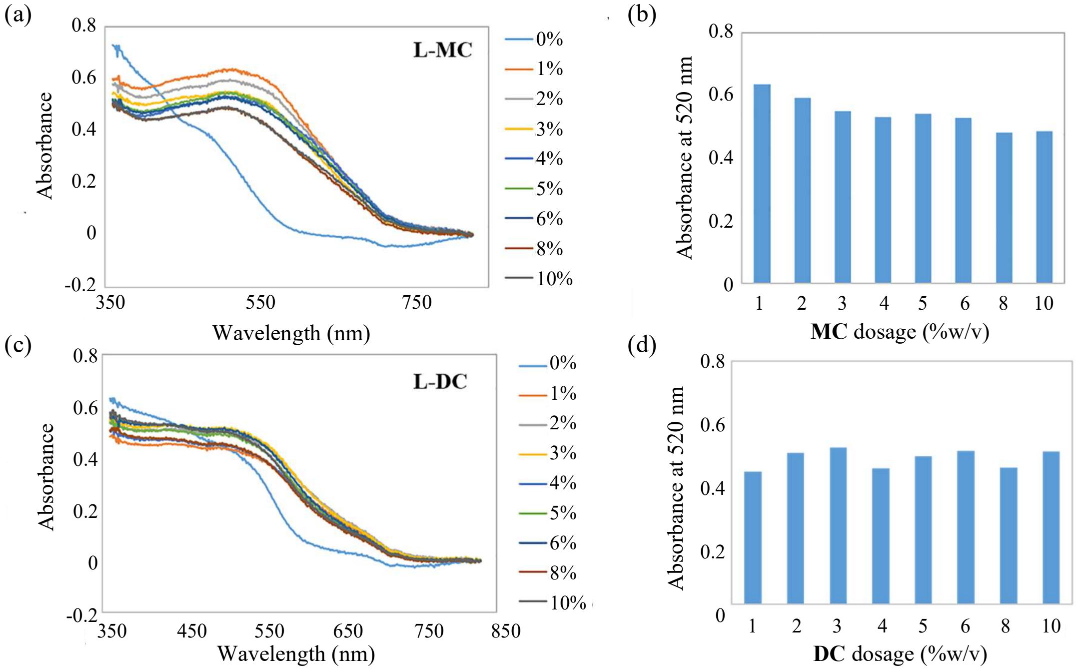


Figure 7. The comparison of UV-Vis DRS spectra (a, c) and the absorbance at 520 nm (b) and 509 nm (d) of the lake pigments from sappan wood prepared by using **MC** and **DC** as the adsorbents.

Table 4. CIELAB of the lake pigments from sappan wood prepared using the different dosage of **MC** and **DC**.

									
MC Dosage (%)	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**8**	**10**
L*	83.21	51.89	52.53	56.95	51.03	51.48	53.99	58.28	56.80
a*	10.15	14.84	13.32	13.71	10.30	11.76	11.48	12.61	11.72
b*	36.06	4.47	4.13	5.20	2.44	3.52	4.03	5.87	5.50
									
DC Dosage (%)	**0**	**1**	**2**	**3**	**4**	**5**	**6**	**8**	**10**
L*	68.89	63.14	56.19	55.43	61.72	57.84	57.22	61.55	58.01
a*	18.93	11.88	13.38	14.43	13.63	14.84	15.42	14.27	15.61
b*	25.82	9.39	9.35	9.88	10.71	11.13	11.29	11.35	12.75

Absorbance

3.2.2 Effect of initial pH on the adsorption

In order to investigate the effect of initial pH of sappan wood extract on the adsorption on clays, the initial pH of sappan wood extracts was varied from 3 to 11, where pH of sappan wood extracts was adjusted using NaOH and HCl. The results showed that there were some differences between the pH of sappan wood extracts before and after the adsorption as illustrated in Table 5. Table 6 and Figure 8 revealed the color, CIELAB and UV-Vis DRS spectra of lake pigments prepared by using different initial pH of sappan wood extracts. It was found that different colors of lake pigments were obtained when different initial pH of sappan wood extracts was used. However, for both **L-MC** and **L-DC**, deeper color with higher UV-Vis DRS absorbance of lake pigments can be obtained when sappan wood extracts at pH 5 and pH 7 were used, compared with those of other pH.

3.2.3 Effect of time on the adsorption

The optimum of adsorption time for the preparation of lake pigments was investigated. Clays were mixed with sappan wood extracts for 10, 20, 40, 60, 120 and 180 min and the CIELAB and UV-Vis DRS of the lake pigments were measured and compared. It was found that although the adsorption times were varied from 10 to 180 min, the color and the CIELAB of the lake pigments were similar as shown in Table 7. Additionally, Figure 9 elucidated that the maximum diffuse reflectance of **L-MC** and **L-DC** prepared by using different adsorption times were similar. This indicated that the adsorption of sappan wood extracts on clays could be completed within 10 min.

Table 5. pH of sappan wood extracts after the adsorption using **MC** and **DC** as the absorbents and different initial pH of sappan wood extracts.

Initial pH	pH of sappan wood extracts after adsorption	
	MC	DC
3	3.05	4.67
5	4.72	6.50
7	5.31	7.03
9	8.20	8.52
11	9.69	10.25

Table 6. CIELAB of the lake pigments from sappan wood prepared using **MC** and **DC** as the absorbents and different initial pH of sappan wood extracts.

 MC					
pH	**3**	**5**	**7**	**9**	**11**
L*	53.47	49.70	51.09	58.00	64.59
a*	7.74	11.77	13.26	13.80	9.55
b*	7.15	3.49	4.05	8.70	12.69
 DC					
pH	**3**	**5**	**7**	**9**	**11**
L*	57.80	53.23	50.65	60.77	60.23
a*	9.26	14.42	14.01	12.27	13.23
b*	9.07	11.73	9.44	13.58	16.83

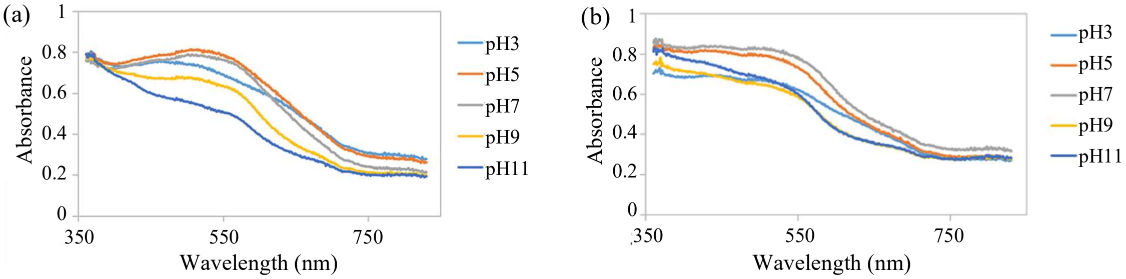


Figure 8. The comparison of UV-Vis DRS spectra of the lake pigments from sappan wood prepared by using **MC** (a) and **DC** (b) as the adsorbents and different initial pH of sappan wood extracts.

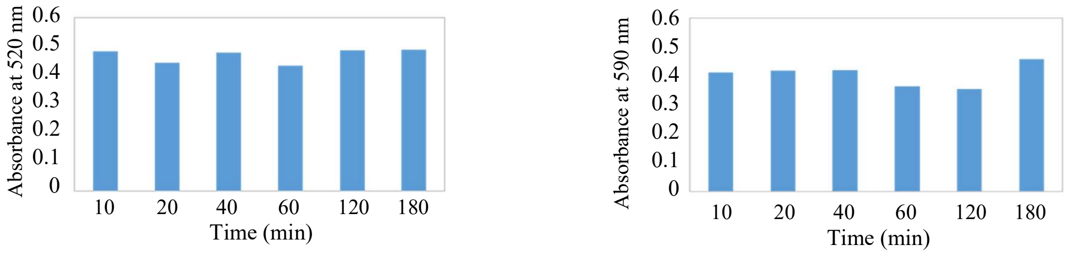
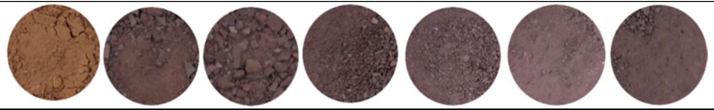


Figure 9. The comparison of the absorbance at the maximum diffuse reflectance of the lake pigments from sappan wood prepared by using **MC** (a) and **DC** (b) as the adsorbents at different adsorption time.

Table 7. CIELAB of the lake pigments from sappan wood prepared using **MC** and **DC** as the absorbents at different adsorption time.

MC							
Time (min)	**0**	**10**	**20**	**40**	**60**	**120**	**180**
L*	83.21	58.20	53.98	54.16	56.73	52.59	52.62
a*	10.15	9.75	10.27	10.93	10.19	9.87	10.25
b*	36.06	6.88	8.05	7.82	6.57	4.61	5.51
DC							
Time (min)	**0**	**10**	**20**	**40**	**60**	**120**	**180**
L*	68.89	55.24	49.64	52.14	54.71	54.20	53.25
a*	18.93	11.49	10.90	11.27	9.44	8.68	12.65
b*	25.82	10.66	10.29	10.53	9.01	8.41	11.60

3.3 Adsorption mechanism

After the adsorption of brazilein, the colors of **MC** and **DC** were changed to that similar to the color of brazilein. This could be due to the metal-brazilein complex formation and electrostatic interaction between the brazilein molecules and the surface of clays [29,30]. The proposed electrostatic interaction between brazilein and clay was shown in Figure 10. Brazilein could act as a chelating ligand coordinated with Si and Al on the surface of clays, which was similar to the proposed chelation of brazilein described in previous works [19,22]. Additionally, there was electrostatic interaction between the the negative dipole on oxygen atoms of brazilein and the positively charged surface of the clay. (the pH_{pzc} values of **MC** and **DC** were 7.60 and 7.94, respectively) [21,31,32]. This proposed adsorption mechanism was also similar to those observed in the previous reports [33-35].

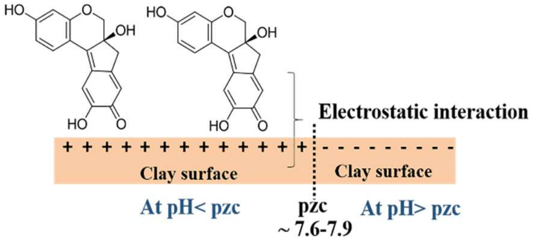


Figure 10. Proposed electrostatic interaction between the brazilein molecules and the surface of the clays.

4. Conclusions

Reddish-brown **L-MC** and **L-DC** were successfully prepared by the simple adsorption method, which required minimum adsorption time of only 10 min. Deep color lake pigments could be obtained when sappan wood extracts at pH 5 or pH 7 were used. The colors of **L-MC** and **L-DC** arose from the complex formation and electrostatic interaction between brazilein and the surface of the clay. Additionally, the physical properties of clays and lake pigments were explored by XRD, SEM, FT-IR, BET, UV-Vis DRS, TGA and CIELAB. The above discussed results could enhance the use of natural clays, which could increase their value and benefit the community in term of optional income.

5. Acknowledgements

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